Consommation et Affaires commerciales Canada
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Consumer and Corporate Affairs Canada
Patent Office

(21) (A1) 2,099,854
(22) 1993/07/05
(43) 1994/01/08

5,070,039

(51) INTL.CL. [5] B32B-015/08; C23C-014/24; B05D-003/02; B05D-005/10; B05D-007/02; B01J-019/08

(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Process for Enhacing Adhesion Between a Metal and a Polymeric Substrate

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(30) (US) 909,907 1992/07/07

(57) 23 Claims

2099854

Abstract of the Disclosure

PROCESS FOR ENHANCING ADHESION BETWEEN A METAL AND A POLYMERIC SUBSTRATE

A process for enhancing adhesion between a metal and a polymeric substrate utilizing a heating process step. In the process, a polymeric substrate is coated with a metal in a vacuum evaporation process. The metal coated substrate is then heated for a predetermined time and temperature to enhance adhesion between the metal and the substrate, without deforming the substrate.

91-3-067

G0311/7033
WRM:PCL:sjd:1500o

PROCESS FOR ENHANCING ADHESION BETWEEN A METAL AND A POLYMERIC SUBSTRATE

Field of the Invention

The present invention pertains to an improved process for enhancing adhesion between a metal and a polymeric substrate.

Description of the Prior Art

Plastics have replaced more traditional materials, such as glass, in many applications for a variety of reasons including better strength, lighter weight, and lower cost. One such application is in metallization processes, wherein plastics are preferred to glass as a substrate material. Metalized plastics are commonly used as reflectors, primarily in automotive headlamps. A variety of polymeric substrates, including polycarbonate and nylon, are commonly used in the production of lighting reflectors. Although several metals have been applied to these plastics, aluminum is currently used in all automotive headlamp reflectors.

Aluminum is commonly applied to a plasma-treated polymer substrate in a vacuum evaporation process. In

the first step of such a process, the plastic substrates are put into a vacuum chamber and exposed to a glow discharge, having an energy sufficient to yield a plasma at the substrate surface. This discharge oxidizes material on the substrate surface and promotes adhesion through a combination of eliminating dirt and other small molecules from the surface, cross-linking the surface, and providing oxygen-containing functional groups with which the subsequently applied aluminum will react. Typically the pressure is then lowered, and the aluminum is evaporated from heated tungsten filaments onto the surface of the substrate to a thickness of approximately 500-1000 angstroms.

Freshly prepared aluminum surfaces have a reflectivity of about 92% over the visible wavelength range. Utilizing a metal having a greater reflectivity would increase the efficiency of a lighting system. For example, silver, one of the best-known reflectors of visible light, which has a reflectivity approaching 98%, could theoretically increase the efficiency of a lighting system by approximately 6% without any changes to the lamp itself.

Additionally, silver is less reflective than aluminum in the ultraviolet. For example, at 320 nanometers silver reflects less than 10% while aluminum reflects 92% This lack of reflectivity in the ultraviolet may be potentially useful in preventing degradation of polymeric lenses by ultraviolet radiation.

Silver, however, has several drawbacks, relative to aluminum, for use in lighting systems. These include

higher cost, and a lack of environmental resistance of the silver surface. In addition, if silver is substituted for aluminum in the existing process of vacuum evaporation, the adhesion of the silver to the surface of the substrate is not adequate. In many cases the initial adhesion is insufficient, and after exposure, as in several specific environmental tests, adhesion decreases.

In automotive applications these tests are of three types. The first test is immersion in water at an elevated temperature, for example, 96 hours in deionized water at 90° F; the second test is exposure to a salt spray at elevated temperature, for example, 48 hours in 5% NaCl at 100°F; the third test is exposure to humid air, for example, 120 hours in 90% relative humidity at 100°F.

It is therefore an object of this invention to provide a process for enhancing adhesion between metals and a polymeric substrate. A further object of the invention is to provide a process for enhancing adhesion between silver and a polymeric substrate.

Summary of the Invention

According to the present invention, a process to enhance adhesion between a metal and a polymeric substrate utilizes a heating process.

In the process of the invention, a polymeric substrate is coated with a metal, deposited by a vacuum evaporation process. The metal coated substrate is then heated for a predetermined time and temperature to

enhance adhesion between the metal and the substrate, without deforming the substrate.

For example, in a preferred embodiment, a silver-coated polycarbonate substrate is heated at temperatures between about 100°C to about 150°C for about 30 to 60 minutes. Temperatures higher than 150°C are impractical due to the softening of the polymer, while temperatures lower than 100°C are less effective at promoting adhesion. After the heating process is completed, greater than 99% of the silver adheres to the polycarbonate substrate during a tape-peel test, performed after exposure to environmental conditions.

Other objects and features of the present invention will become apparent from the following detailed description.

Detailed Description of the Invention

The present invention provides a process for promoting adhesion between a metal and a polymeric substrate.

In the process of the invention, a polymeric substrate is placed into a reaction chamber wherein the pressure is lowered, and a metal is vaporized. The polymeric substrate is then exposed to the metal vapor, and the metal is deposited on the substrate. The metal coated substrate is then heated for a predetermined time and temperature to promote adhesion between the metal and the substrate, without deforming the substrate.

While the process of the present invention may be used to produce various products, of particular interest

is the production of reflectors and, more specifically, automotive headlamp reflectors. Typically, various polymers are used in this application, including polycarbonate and nylon. Most preferably, polycarbonate is used as the polymeric substrate due to its light weight, high impact strength, moldability and rigidity. It should be noted that various other polymers, in addition to those used for automotive headlamp reflectors, may be utilized in the process of the present invention to produce a variety of metalized products, including, for example polypropylene, polymethyl methacrylate, high density polyethylene, polyethylene terephthalate, acrylic, and phenolic resins.

Once molded into the desired shape, the polymeric substrate may be cleaned with soap and water and/or plasma treated. Typically, a substrate to be plasma treated is placed into a reaction chamber and exposed to a glow discharge having an energy sufficient to yield a plasma. At reduced pressures, glow discharges may be produced by the use of a high frequency, such as radio or microwave frequency, alternating current passed through a coil surrounding the chamber, or between two external electrodes attached to the chamber. This discharge excites molecules within the chamber which oxidize the substrate's surface. Typically, any gas, such as oxygen, nitrogen, or air, may be used within the chamber; in the present embodiment, the air present in the chamber is used to oxidize material on the substrate surface. The excited molecules on the substrate's surface promote adhesion by cleaning the surface of

dirt, and perhaps other small molecules, cross-linking the surface molecules, and providing oxygen-containing functional groups.

The plasma may alternatively be formed from a corona discharge. A corona discharge may occur at any pressure and in all types of gases. This discharge is physically similar to a glow discharge in a highly non-uniform electric field. The electric energy in a corona discharge is converted chiefly into heat in the gas within the chamber.

After the polymeric substrate is cleaned and/or exposed to the plasma treatment, the pressure in the reaction chamber is lowered from about 1×10^{-2} mbar to about 1×10^{-4} mbar. In the low pressure atmosphere the metal is evaporated, and is subsequently deposited on the surface of the substrate.

Many different types of metals may be used in the process of the present invention. However, for automotive headlamp reflectors, an important feature to be considered when selecting metals is reflectivity. Possible metals include copper, aluminum, gold and silver. Of these, silver, when freshly deposited, is the best reflector of visible light known, and is therefore the most preferred metal coating.

The metal coatings are formed by condensation of metal vapor. Typically, a metal holder is positioned on a filament, which is connected to electrodes. A current is passed through the filament to vaporize the metal which is placed into the metal holder. Typically, the metal holder is constructed of a material which has a

higher melting point than the metal to be vaporized, and which will not react with the selected metal during the process. Preferably, the holder material is tungsten, molybdenum, tantalum or a ceramic material. Most preferably, a tungsten filament is used for heating. In the chamber, the filament, and therefore the vaporizing metal, is typically within three feet of the polymeric substrate material. Most preferably, the vaporizing metal is within two feet of the substrate; a relatively short distance is preferred due to the nature of the vaporized metal atoms which are deposited upon everything in their path while being transferred from the filament to the substrate.

A quartz crystal monitor, positioned at the same distance from the vaporizing metal as the substrate, is used to determine the transfer rate of the vaporized metal. Typical thin metal film deposition rates are between about 1 to 20 angstroms per second. A relatively fast metal deposition rate, of about 10 angstroms per second, is preferred to prevent impurities from being deposited with the metal onto the substrate. By adjusting the voltage applied to the filament, any desired deposition rate may be achieved. Generally, these rates do not vary with the substrate temperature.

The quartz crystal monitor is also used to determine the total amount, or thickness, of the metal deposited on the substrate. To provide adequate reflectivity a thickness of at least 500 angstroms is required, as metal thicknesses less then 500 angstroms are often transparent. Further, although a vacuum evaporation

process may be used to deposit metal coatings of a thickness of up to one micron, at that thickness the stress may be too high, and cracks in the coating surface may occur. A preferred thickness of the metal coating upon the substrate is between about 500 angstroms and about 1000 angstroms. When the quartz crystal monitor determines that a desired metal thickness is achieved, the process may be stopped, by blocking the path of the metal vapor to the substrate mechanically, or by shutting off the voltage applied to the filaments, or by burning out (evaporating) all of the metal.

When the desired thickness of the metal coating is deposited upon the polymeric substrate, and the deposition process is terminated, the metal coated polymeric substrate is removed from the chamber and is placed into an oven. Typically, the heating process is carried out in an air atmosphere; other gases however, such as nitrogen, may be present. Depending on the polymeric substrate chosen, the metal coated substrate is heated for a predetermined time and temperature to enhance the adhesion between the metal and the substrate. Polycarbonate substrates, for example, are heated at temperatures between about 100°C to about 150°C for about 30 to 60 minutes. Temperatures higher than 150°C are impractical due to the softening of the polymer, while temperatures lower than 100°C are less effective. The most preferred heating temperature for polycarbonate and silver is about 130°C for about one hour. Polyetherimide substrates generally require

higher temperatures of about 200°C for periods of about 30 minutes to promote adhesion between the metal and the substrate.

It is believed that the heating process step utilized in the present invention enhances the adhesion of a metal to a polymeric substrate by either reorganizing the chains of the substrate, which results in better contact between the metal and the polymer, or by inducing a physical or chemical reaction between the metal and the polymer.

The present invention will be further illustrated by the following examples which are intended to be illustrative in nature and are not to be construed as limiting the scope of the invention.

Example I

The adhesion of silver to a polycarbonate substrate was compared with the adhesion of aluminum to a polycarbonate substrate, utilizing the known vacuum evaporation process, without the subsequent heating process. The experimental results are presented in Table 1.

The first samples were not cleaned prior to testing; the second samples were cleaned by scrubbing with soap and water, and were then dried prior to testing; and the third samples were similarly cleaned, and subjected to an air plasma (which simulates the glow discharge used in the above-described commercial process). The adhesion was tested first, initially after the vacuum

evaporation process, and second, after water immersion for 18 hours at 25°C. A "Pass" means that when adhesive tape (Permanent Mending Tape 3M Corporation, St. Paul, MN) is applied to the metalized substrate, which has been scored with a razor blade into a 1 centimeter square grid, and then peeled up, less than 1% of the silver peeled off the surface with the tape. The percentage indicated in failed samples is that portion of the silver that peeled up.

TABLE 1

A. Silver Adhesion

Sample	Substrate	Initial Adhesion	After Water Immersion (18h, 25°C)
1.	Polycarbonate	Fail (80%)	Fail (80%)
2.	Polycarbonate (Cleaned).	Fail (70%)	Fail (90%)
3.	Polycarbonate (Cleaned then Air Plasma)	Fail (90%)	Fail (100%)

B. Aluminum Adhesion

Sample	Substrate	Initial Adhesion	After Water Immersion (18h, 25°C)
1.	Polycarbonate	Pass	Fail (100%)
2.	Polycarbonate (Cleaned).	Pass	Fail (100%)

3.	Polycarbonate (Cleaned then Air Plasma)	Pass	Pass

This experiment shows that when silver is substituted for aluminum in a standard vacuum evaporation process, adhesion is not adequate initially and is less adequate after water immersion. It is also noted that aluminum adhesion is enhanced by utilizing the air plasma prior to the vacuum evaporation process.

Example II

A silver coated polycarbonate substrate, prepared with a cleaned, but not plasma treated, polycarbonate sheet (such as Sample 2, Example I) in a vacuum evaporation process, was heated to permit better interaction between the metal and the substrate and to enhance overall adhesion. The experimental results are presented in Table 2.

The samples were subjected to various temperatures for various periods to determine the optimum bake conditions to improve adhesion of silver deposited by a vacuum evaporation process onto a polycarbonate substrate. After the heating process, the samples were scored into a 1 centimeter square grid with a razor blade and exposed to deionized water, at 90°F for 96 hours, before being dried and subjected to a tape peel test. A "pass" indicates that less than 1% of the silver peeled off of the surface with the tape.

TABLE 2

Sample	Bake Conditions	Post-Environment Tape Peel Test
1.	None	Fail
2.	50°C, 1h	Fail
3.	100°C, 1h	Fail
4.	130°C, 1h	Pass
5.	150°C, 30 min	Sample distorted in oven

This data shows that the polycarbonate substrate exhibits improved adhesion to silver, deposited by vacuum evacuation, when heated for one hour at 130°C (Sample 4). Temperatures of 100°C or less failed the tape peel test, while temperatures of 150°C or higher softened the polymer.

Example III

The experiment run in Example II was repeated to determine the optimum heating process time necessary at a given temperature. The experimental results are presented in Table 3.

TABLE 3

Sample	Bake Conditions	Post-Environment Tape Peel Test
1.	None	30% Silver Loss
2.	130°C, 1 min	20% Silver Loss
3.	130°C, 5 min	5% Silver Loss
4.	130°C, 30 min	5% Silver Loss
5.	130°C, 60 min	Pass (<1% Silver Loss)
6.	130°C, 135 min	Pass

The polycarbonate substrate appears to require greater than 30 minutes at 130°C to insure passing the tape peel test. Note also that periods of up to 135 minutes at 130°C resulted in less than 1% silver loss.

Example IV

Experiments for other polymeric substrates demonstrate that the trend of Examples II and III is a general one. Polyetherimide silver coated substrates, prepared similarly to the polycarbonate samples of Sample 2, Example I in a vacuum evaporation process, pass the tape peel test after water immersion (as described in Example I) without being subjected to any post deposition heating process. The samples, however, do not pass the tape peel test after being subjected to a 5% salt spray at 100°F for 48 hours. The experimental

results are presented in Table 4.

TABLE 4

Sample	Bake Conditions	Post-Environment Tape Peel Test
1.	None	75% Silver Loss
2.	200°C, 1h	15% Silver Loss
3.	200°C, 4h	Silver Surface Damage

These results show that exposure to heat (Sample 2. 200°C for one hour) increases the adhesion of silver to the polyetherimide substrate, as the silver loss was decreased from 75% to 15% after exposure to the salt spray.

Example V

Samples of polyetherimide typically require cleaning before metal deposition to obtain optimum adhesion results. However a post-deposition heating process can effectuate similar results. Polyetherimide silver coated substrates, prepared similarly to those in Example IV, were subjected to a post deposition heating process. The samples were then exposed to deionized water at 90°F for 96 hours before being dried and subjected to a tape peel test. Experimental results are presented in Table 5.

TABLE 5

	Sample	Bake Conditions	Post-Environment Tape Peel Test
1.	Cleaned	None	Pass (<1% silver loss)
2.	Cleaned	200°C 1h	Pass
3.	Not Cleaned	None	40 - 100% Silver Loss)
4.	Not Cleaned	130°C, 1h	10% Silver Loss
5.	Not Cleaned	200°C, 30 min	Pass

The above results show that a cleaned polyetherimide substrate does not require the post-deposition heating to pass the tape peel test after being subjected to the water immersion test described above. Similar results are obtained when the clean sample is subjected to a post-deposition heating process. However, when the polyetherimide sample is not cleaned or subjected to a post-deposition hearing process the sample fails the tape peel test. Further, while the heating cycle of 130°C for one hour provided sufficient adhesion between the polycarbonate substrate and silver to pass the water immersion test (see Example II, Table 2), it is not sufficient for use with polyetherimide. An unclean sample of a polyetherimide substrate requires temperatures of about 200° for a period of about 30 minutes to pass the tape peel test. This test confirms that the amount of heating required depends on the nature of the polymeric substrate chosen.

Example VI

The experiment run in Example II was repeated using copper coated (1000 angstroms thick) polycarbonate substrates and gold coated (1000 angstroms thick) polycarbonate substrates to observe whether heating would enhance overall adhesion of polycarbonate to metals other than silver. The experimental results are presented in Table 6.

The samples were not subjected to any additional environmental test conditions after the heating process. After heating, the samples were scored into a 1 centimeter square grid with a razor blade and subjected to a tape peel test. A "pass" indicates that less than 1% of the metal coating peeled off the surface with the tape. The percentage indicated in failed samples is that portion of the metal which peeled up.

TABLE 6

Sample	Metal	Bake Conditions	Post-Environment Tape Peel Test
1.	Gold	None	Fail (100%)
2.	Gold	130°C, 1 h	Fail (15%)
3.	Gold	130°C, 18 h	Fail (1%)
4.	Copper	None	Fail (100%)
5.	Copper	130°C, 1 h	Pass

6.	Copper	130°C, 5 min	Pass
7.	Copper	130°C, 1 min	Fail (1%)
8.	Copper	130°C, 30 sec	Fail (10%)

This data shows that the polycarbonate substrate exhibits improved adhesion to gold and copper, deposited by vacuum evaporation, when heated for a period of time. Gold adhesion improved with time, and approached passing at a period of 18 hours at 130°C. Higher temperatures are not practical (as shown in Example II). Copper adhesion also improved with time; at a temperature of 130°C the copper coated polycarbonate substrate passed the tape peel test when heated for at least 5 minutes.

Although particular embodiments of the invention have been described in detail for purposes of illustration, various modifications may be made without departing from the spirit and scope of the present invention. Accordingly, the invention is not to be limited except at by the amended claims.

CLAIMS

What is claimed is:

1. A process comprising:
depositing a metal coating onto a polymeric substrate; and
heating said metal coated substrate for a predetermined time and temperature sufficient to enhance adhesion between said metal and said substrate, without deforming said substrate.

2. The process as claimed in claim 1 wherein said polymeric substrate is selected from the group consisting of polycarbonate, polyetherimide, and nylon.

3. The process as claimed in claim 1 wherein said polymeric substrate is polycarbonate.

4. The process as claimed in claim 1 wherein said polymeric substrate is polyetherimide.

5. The process as claimed in claim 1 wherein said polymeric substrate is exposed to a glow discharge having an energy sufficient to yield a plasma at the substrate surface, prior prior to depositing said metal.

6. The process as claimed in claim 1 wherein said metal is selected from the group consisting of silver, gold, aluminum, and copper.

7. The process as claimed in claim 1 wherein said metal is silver.

8. The process as claimed in claim 1 wherein said metal is deposited by vacuum evaporation at a pressure of about 1 X 10^{-4} mbar.

9. The process as claimed in claim 3 wherein said metal coated substrate is heated for a period of at least about 30 minutes, at a temperature of between about 100°C to about 150°C.

10. The process as claimed in claim 4 wherein said metal coated substrate is heated for a period of about 30 minutes at a temperature of about 200°C.

11. The process as claimed in claim 1 wherein said metal coating is between about 500 angstroms to about 1000 angstroms thick.

12. The process as claimed in claim 1 wherein greater than 99% of said deposited metal adheres to said polymeric substrate when the metal is subjected to a tape peel test.

13. In a process for coating a polymeric substrate with silver, the improvement comprising:

heating said silver coated substrate for a predetermined time, at a predetermined temperature, sufficient to enhance adhesion between said silver and

said substrate, without deforming said substrate.

14. The process as claimed in claim 13 wherein said polymeric substrate is selected from the group consisting of polycarbonate, polyetherimide, and nylon.

15. The process as claimed in claim 13 wherein said polymeric substrate is polycarbonate.

16. The process as claimed in claim 15 wherein said silver coated substrate is heated for a period of at least about 30 minutes, at a temperature of between about 100°C to about 150°C.

17. The process as claimed in claim 13 wherein said polymeric substrate is polyetherimide.

18. The process as claimed in claim 17 wherein said silver coated substrate is heated for a period of about 30 minutes at a temperature of about 200°C.

19. The process as claimed in claim 13 wherein said silver coating is between about 500 angstroms to about 1000 angstroms thick.

20. A process comprising:

depositing a silver coating onto a polycarbonate substrate by vacuum evaporation at a pressure of about 1×10^{-4} mbar; and

heating said silver coated substrate for a period of

at least about 30 minutes, at a temperature of between about 100°C to about 150°C to enhance adhesion between said silver and said substrate, without deforming said substrate.

21. A process comprising:

depositing a silver coating onto a polyetherimide substrate by vacuum evaporation at a pressure of about 1×10^{-4} mbar; and

heating said silver coated substrate for a period of at least about 30 minutes, at a temperature of about 30 minutes at a temperature of about 200°C to enhance adhesion between said silver and said substrate, without deforming said substrate.

22. An article comprising a polymeric substrate and a silver layer; wherein said polymeric substrate is selected from the group consisting of polycarbonate, polyetherimide, and nylon; wherein said silver layer has a thickness of between about 500 angstroms to about 1000 angstroms; and wherein greater than 99% of said silver layer adheres to said polymeric substrate when the silver layer is subjected to a tape peel test.

23. Each and every novel feature or novel combination of features herein disclosed.

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PATENT AGENT FOR THE APPLICANT

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente